

What is claimed is:

1. A process for protecting an aluminum substrate or a steel substrate against corrosion comprising:

5 providing an aluminum or steel surface to be protected,

applying to said surface a protective composition comprising of a corrosion inhibitor composition, said protective composition being formed by  
10 reacting an organic compound from a group consisting of di-mercapto and poly-mercapto derivatives and their derivatives, with a cationic species selected from a group consisting of Bi(III), Co(II), Cd(II), Pb(II), Ag(I), Sb(III), Cu(II), Ni(II), Li(I), La(III), Al(III),  
15 and Pr(III), said protective corrosion inhibitor composition having a limited solubility in water of between about 0.01 and about 1000 mmols/ per liter of water.

2. A process according to claim 1 wherein  
20 said protective composition is applied as a layer of less than approximately 20 microns in thickness.

3. A process according to claim 1 wherein said protective composition has a limited solubility in water of between about 0.1 and about 10 mmols/ liter.

25 4. A process according to claim 1 wherein said protective composition is applied as an aqueous solution and is subsequently dried whereby a conversion coating is formed on said substrate, said conversion coating being subsequently coated with a paint.

30 5. A process according to claim 1 wherein said protective composition is incorporated into a silane-based gel coating.

6. A process according to claim 1 wherein said protective corrosion inhibitor composition is  
35 selected from the group consisting of 2,5-dimercapto-1,3,4 thiadiazole or (DMTD), 2,4-dimercapto-s-triazolo-[4,3-b]-1,3-4-thiadiazole, trithiocyanuric acid or (TMT),

derivatives of DMTD, and derivatives of TMT, dithiocyanuric acid, dimercaptopyridine, 2,4-dithiohydantoine, and 2,4-dimercapto-6-amino-5-triazine.

5        7. A process according to claim 1 wherein said protective composition is selected from the group consisting of  $M(\text{DMTD})_n$  where  $n = 1, 2$  or  $3$ , and  $M$  is a metal cation selected from the group consisting of Bi, Co, Ni, Cd, Pb, Ag, Sb, Al, Li, La, Pr, or Cu; aryl ammonium salts of DMTD; aryl ammonium salts of  $(\text{DMTD})_n$ ;  
10       quaternary ammonium salts of DMTD; quaternary ammonium salts of  $(\text{DMTD})_n$ ; polyaniline, polythiophen, and polypyrrol doped with DMTD; polyaniline, polythiophen, and polypyrrol doped with  $(\text{DMTD})_2$ ; and micro and nano composites of poly DMTD/polyaniline, DMTD/polythiophen  
15       and poly DMTD/polypyrrol.

8. A process according to claim 1 wherein said protective composition is applied by incorporating the same in a curable polymeric coating composition and applying said composition over said substrate.

20       9. A process according to claim 1 wherein said protective composition is selected from the group consisting of: N- or S- and N-, N-, S- and N-, S-substituted derivatives of DMTD such as 5-mercapto-3-phenyl-1,3,4-thiadiazoline-2-thione (Bismuthiol II),  
25       substituted derivatives of 5,5' dithio-bis(1,3,4 thiadiazole-2(3H)-thione  $(\text{DMTD})_2$ , substituted derivatives of 5,5'-Thiobis (1,3,4-thiadiazole-2(3H)-thione substituted derivatives of dimercaptopyridine, and of 2,4-dithiohydantoine, substituted derivatives of 2,4-dimercapto-6-amino-5-triazine and  $(\text{DMTD})_n$ , a polymer of  
30       DMTD; a salt of DMTD of general formula,  $M(\text{DMTD})_n$ , where  $n = 1, 2$  or  $3$ , and  $M$  is a metal cation and  $M = \text{Bi, Co, Ni, Cd, Pb, Ag, Sb, Li, La, Pr, Al or Cu}$ ; a salt of  $(\text{DMTD})_n$  of general formula  $M[(\text{DMTD})_n]_m$ , where  $n=2$  or  $n>2$ ,  $m=1, 2$ ,  
35       or  $3$  and  $M = \text{Bi, Co, Ni, Cd, Pb, Ag, Sb, Li, La, Pr, Al or Cu}$ ; aryl ammonium salts of DMTD and  $(\text{DMTD})_n$ ; quaternary ammonium salts of DMTD and  $(\text{DMTD})_n$ ;

polyammonium salts of DMTD and (DMTD)<sub>n</sub> formed with a polyamine; polyaniline, polypyrrole and polythiophen doped with DMTD; polyaniline, polypyrrole and polythiophen doped with (DMTD)<sub>2</sub>; micro and nano composites of poly DMTD/polyaniline, poly DMTD/polypyrrole, and poly DMTD/polythiophen; DMTD, salts of DMTD, and derivatives of DMTD, as constituents of an inorganic matrix; and a combination of said forms.

10. A process according to claim 1 wherein said protective composition is selected from the group consisting of:

S-substituted derivatives of trithiocyanuric acid (TMT); a salt of TMT of general formula, M(TMT)<sub>n</sub>, where n = 1, 2 or 3, and M is a metal cation and M = Bi, Co, Ni, Cd, Pb, Ag, Sb, Li, La, Pr, Al, or Cu; aryl ammonium salts of TMT; quaternary ammonium salts of TMT; polyamines formed with TMT; polyaniline doped with TMT; polypyrrole and polythiophen doped with TMT; micro and nano composites of poly TMT/polyaniline, poly TMT/polypyrrole, and poly TMT/polythiophen; TMT, salts of TMT; and derivatives of TMT, as constituents of an inorganic matrix; salts of TMT and derivatives of TMT in encapsulated form in a polymer matrix, or as a cyclodextrin-inclusion compound; and a combination of said forms.

11. The protective composition of claim 1 wherein the protective composition is used in a paint.

12. The steel substrate of claim 1, wherein said steel substrate comprises a galvanized steel.

13. A method for producing a protective corrosion inhibitor composition, the method comprising:

incorporating an organic compound selected from the group consisting of DMTD, TMT, derivatives of DMTD, and derivatives of TMT, with an inorganic compound selected from the group consisting of phosphates, molybdates, borates, silicates, tungstates, phosphotungstates, phosphomolybdates, cyanamides,

carbonates, SiO<sub>2</sub> and mixtures thereof.

14. The method according to claim 13, wherein said inorganic compound consists of a Ce-molybdate, La-molybdate, Zn-molybdate, or a mixture thereof.

5 15. An atmospheric corrosion inhibitor for a steel substrate, said corrosion inhibitor formed by:

reacting an organic compound from a group consisting of di-mercapto and poly-mercapto derivatives and their derivatives, with an ionic species from a group  
10 consisting of Bi(III), Co(II), Cd(II), Pb(II), Ag(I), Sb(III), Cu(II), Ni(II), Li(I), La(III), Al(III)), and Pr(III).

16. An atmospheric corrosion inhibitor for aluminum, said corrosion inhibitor formed by:

15 reacting an organic compound from a group consisting of TMT and TMT derivatives, with species of Bi(III), Co(II), Cd(II), Pb(II), Ag(I), Sb(III), Cu(II), Ni(II), Li(I), La(III), Al(III), and Pr(III).

17. A process for protecting an aluminum  
20 substrate or a steel substrate against corrosion comprising:

providing an aluminum or steel surface to be protected,

applying to said surface a protective  
25 composition comprising of a corrosion inhibitor composition, said protective composition being formed by reacting an organic compound from a group consisting of di-mercapto and poly-mercapto derivatives and their derivatives, with a cationic species selected from a  
30 group consisting of Zn(II), Fe(II), Ca(II), Sr(II), Mg(II), Ce(III), Al(III), and Zr(IV), said protective corrosion inhibitor composition having a limited solubility in water of between about 0.01 and about 1000 mmoles/ per liter of water.

35 18. A process according to claim 17 wherein said protective composition is selected from the group consisting of 2,5-dimercapto-1,3,4 thiadiazole (DMTD),

2,4-dimercapto-s-triazolo-[4,3-b]-1,3,4-thiadiazole,  
trithiocyanuric acid (TMT), derivatives of DMTD, and  
derivatives of TMT, dithiocyanuric acid,  
dimercaptopyridine, 2,4-dithiohydantoine, and 2,4-  
5 dimercapto-6-amino-5-triazine.

19. A process according to claim 17 wherein  
said protective composition is selected from the group  
consisting of 2,5-dimercapto-1,2,4 thiadiazole; 2,4-  
dimercapto-s-triazolo-[4,3-b]-1,3,4-thiadiazole; 5,5'  
10 dithio-bis (1,3,4 thiadiazole-2(3H) - thione(DMTD)<sub>2</sub>;  
5,5'-Thiobis(1,3,4-thiadiazole-2(3H)-thione;  
dimercaptopyridine, and 2,4-dithiohydantoine, and 2,4-  
dimercapto-6-amino-5-triazine and 5-mercapto-3-phenyl-  
1,3,4-thiadiazoline-2-thione (Bismuthiol II), (DMTD)<sub>n</sub> and  
15 M(DMTD)<sub>n</sub>, where n = 1,2 or 3 and M is a metal cation  
selected from the group consisting Zn, Fe, Ca, Sr, Mg,  
Ce, and Zr; and alkyl ammonium salts of (DMTD)<sub>n</sub>.

20. A process according to claim 17 wherein  
said protective composition is selected from the group  
20 consisting of:

2,5-dimercapto-1,3,4 thiadiazole (DMTD); 2,4-  
dimercapto-s-triazolo-[4,3-b]-1,3,4-thiadiazole; an  
organic derivative of DMTD such as 5-mercapto-3-phenyl-  
1,3,4-thiadiazoline -2-thione (Bismuthiol II), a salt of  
25 DMTD of general formula, M(DMTD)<sub>n</sub>, where n = 1,2 or 3,  
and M = Zn, Fe, Ca, Sr, Mg, Ce, Al, or Zr, a salt of  
(DMTD)<sub>n</sub> of general formula M[(DMTD)<sub>n</sub>]<sub>m</sub>, where n=2 or n>2,  
m=1,2, or 3, salts of DMTD ,and derivatives of DMTD in  
encapsulated form in a polymer matrix, or as a  
30 cyclodextrin-inclusion compound; and a combination of  
said forms.

21. A process according to claim 17 wherein  
said protective composition is selected from the group  
consisting of:

35 trithiocyanuric acid (TMT), M(TMT)<sub>n</sub>, where n =  
1,2 or 3, and M = Zn, Fe, Ca, Sr, Mg, Ce, Al, or Zr, and  
derivatives of TMT, as constituents of an inorganic

matrix; and derivatives of TMT in an encapsulated form in a polymer matrix, or as a cyclodextrin-inclusion compound; and a combination of said forms.

22. A process according to claim 17 wherein  
5 said protective composition is selected from the group consisting of:

S-substituted derivatives of trithiocyanuric acid (TMT); a salt of TMT of general formula  $M(TMT)_n$ , where  $n = 1, 2, \text{ or } 3$ , and  $M$  is a metal cation and  $M = \text{Zn, Fe, Ca, Sr, Mg, Ce, Al, or Zr}$ ; aryl ammonium salts of  
10 TMT; quaternary ammonium salts of TMT; polyamine salts formed with TMT; polyaniline doped with TMT; polypyrrole and polythiophen doped with TMT; micro and nano composites of poly TMT/polyaniline, poly TMT/polypyrrole,  
15 and poly TMT/polythiophen; TMT, salts of TMT and derivatives of TMT, as constituents of an inorganic matrix; salts of TMT and derivatives of TMT in encapsulated form in a polymer matrix, or as a cyclodextrin-inclusion compound; and a combination of  
20 said forms.

23. A process according to claim 17 wherein said protective composition is selected from the group consisting of: N- or S- and N-, N-, S- and N-, S-substituted derivatives of DMTD such as 5-mercapto-3-phenyl-1,3,4-thiadiazoline-2-thione (Bismuthiol II),  
25 substituted derivatives of 5,5' dithio-bis(1,3,4 thiadiazole-2(3H)-thione  $(DMTD)_2$ , substituted derivatives of 5,5'-Thiobis (1,3,4-thiadiazole-2(3H)-thione substituted derivatives of dimercaptopyridine,  
30 substituted derivatives of 2,4-dithiohydantoine, substituted derivatives of 2,4-dimercapto-6-amino-5-triazine and  $(DMTD)_n$ , a polymer of DMTD; a salt of DMTD of general formula,  $M(DMTD)_n$ , where  $n = 1, 2 \text{ or } 3$ , and  $M$  is a metal cation and  $M = \text{Zn, Fe, Ca, Sr, Mg, Ce, or Zr}$ ; a  
35 salt of  $(DMTD)_n$  of general formula  $M[(DMTD)_n]_m$ , where  $n=2$  or  $n>2$ ,  $m=1, 2, \text{ or } 3$  and  $M = \text{Zn, Fe, Ca, Sr, Mg, Ce, Al or Zr}$ ; aryl ammonium salts of DMTD and  $(DMTD)_n$ ; quaternary

ammonium salts of DMTD and  $(DMTD)_n$ ; polyammonium salts of DMTD and  $(DMTD)_n$  formed with a polyamines; polyaniline, polypyrrole and polythiophen doped with DMTD; polyaniline, polypyrrole and polythiophen doped with  $(DMTD)_2$ ; micro and nano composites of poly DMTD/polyaniline, poly DMTD/polypyrrole, and poly DMTD/polythiophen; DMTD, salts of DMTD, and derivatives of DMTD, as constituents of an inorganic matrix; and a combination of said forms.

24. A process according to claim 17 wherein said protective composition is selected from the group consisting of:

S-substituted derivatives of trithiocyanuric acid (TMT); a salt of TMT of general formula  $M(TMT)_n$ , where  $n = 1, 2, \text{ or } 3$ , and M is a metal cation and  $M = \text{Zn, Fe, Ca, Sr, Mg, Ce, or Zr}$ ; aryl ammonium salts of TMT; quaternary ammonium salts of TMT; polyamine salts formed with TMT; polyaniline doped with TMT; polypyrrole and polythiophen doped with TMT; micro and nano composites of poly TMT/polyaniline, poly TMT/polypyrrole, and poly TMT/polythiophen; TMT, salts of TMT and derivatives of TMT, as constituents of an inorganic matrix; salts of TMT and derivatives of TMT in encapsulated form in a polymer matrix, or as a cyclodextrin-inclusion compound; and a combination of said forms.

25. A process according to claim 17 wherein said protective corrosion inhibiting composition is applied as an aqueous solution and is subsequently dried whereby a conversion coating is formed on said substrate, said conversion coating being subsequently coated with a paint.

26. A process according to claim 17 wherein said protective composition is incorporated into a silane-based gel coating.

27. An atmospheric corrosion inhibitor for a steel substrate, said corrosion inhibitor formed by:  
reacting an organic compound from a group

consisting of di-mercapto and poly-mercapto derivatives and their derivatives, with an ionic species from a group consisting of Zn(II), Fe(II), Ca(II), Sr(II), Mg(II), Ce(III), Al(III), and Zr(IV).

5                   28. An atmospheric corrosion inhibitor for aluminum, said corrosion inhibitor formed by:

                  reacting an organic compound from a group consisting of TMT and TMT derivatives, with species of Zn(II), Fe(II), Ca(II), Sr(II), Mg(II), Ce(III), Al(III),  
10                   and Zr(IV).

                  29. A method of synthesizing a conductive polymer dope with thio-organic compounds with acidic character, such as DMTD, the method including the steps of:

15                   providing a conductive polymer selected from the group consisting of polyaniline, polypyrrole, and polythiophen, and combinations thereof;

                  providing a thio-organic compound of acidic character selected from a group consisting of di-mercapto and poly-mercapto compounds and their derivatives;  
20                   

                  adding said conductive polymer into a first aqueous solution;

                  deprotonating said conductive polymer in said first aqueous solution; and

25                   reprotonating in a second aqueous solution said deprotonated polymer in the presence of said thio-organic compound of acidic character.

                  30. The method according to claim 29 wherein said thio-organic compound is selected from the group consisting of:  
30

                  2,5-dimercapto-1,3,4 thiadiazole (DMTD), 2,4-dimercapto-s-triazolo-[4,3-b]-1,3,4-thiadiazole, N- or S- and N-, N-, S- and N-, S- substituted derivatives of DMTD such as 5-mercapto-3-phenyl-1,3,4-thiadiazoline -2-thione (Bismuthiol II) and 5,5' dithio-bis(1,3,4  
35                   thiadiazole-2(3H)-thione (DMTD)<sub>2</sub>, and 5,5'-Thiobis(1,3,4-thiadiazole-2(3H)-thione and dimercaptopyridine, and 2,4-



dithiohydantoine, and 2,4-dimercapto-6-amino-5-triazine and (DMTD)<sub>n</sub>, a polymer of DMTD and trithiocyanuric acid TMT.

5 31. A method of synthesizing a conductive polymer doped with thio-organic compounds with acidic character, such as DMTD, the method including the steps of:

10 providing a conductive polymer selected from the group consisting of, polyaniline, polypyrrole, and polythiophen and combinations thereof;

providing an thio-organic compound selected from a group consisting of di-mercapto and poly-mercapto compounds with acidic character and their the derivatives;

15 providing a first aqueous solution containing a base;

adding said conductive polymer to said first aqueous solution;

20 forming a base polymeric compound from said conductive polymer in said first aqueous solution;

providing a second aqueous solution containing a thio-organic compound with acidic character;

adding said base polymer compound to said second aqueous solution; and

25 stirring said thio-organic compound with acidic character and said base polymer compound in said second aqueous solution to form said conductive polymer by re-protonation.

30 32. The method according to claim 31 further including the step of:

adjusting the pH of said first aqueous solution by adding a base.

33. The method according to claim 32 wherein said pH being adjusted to between 9 and 10.

35 34. The method according to claim 31 wherein said second aqueous solution is heated to between 30°C and 95°C during re-protonation.

35. The method according to claim 31 wherein said second aqueous solution contains ethanol from 3% to 50%.

5 36. The method according to claim 31 wherein said thio-organic acid compound is selected from the group consisting of:

2,5-dimercapto-1,3,4 thiadiazole (DMTD), 2,4-dimercapto-s-triazolo-[4,3-b]-1,3,4-thiadiazole, N- or S- and N-, N-, S- and N-, S- substituted derivatives of DMTD  
10 such as 5-mercapto-3-phenyl-1,3,4-thiadiazoline -2-thione (Bismuthiol II), substituted derivatives of 5,5' dithio-bis(1,3,4 thiadiazole-2(3H)-thione (DMTD)<sub>2</sub>, substituted derivatives of 5,5'-Thiobis( 1,3,4-thiadiazole-2(3H)-thione and dimercaptopyridine,  
15 substituted derivatives of 2,4-dithiohydantoin, substituted derivatives of 2,4-dimercapto-6-amino-5-triazine and (DMTD)<sub>n</sub>, a polymer of DMTD and trithiocyanuric acid TMT.